

## Studies of Polarised Ethylenes

### Part V.\* Ultraviolet Spectra; Experimental Results and PPP Calculations

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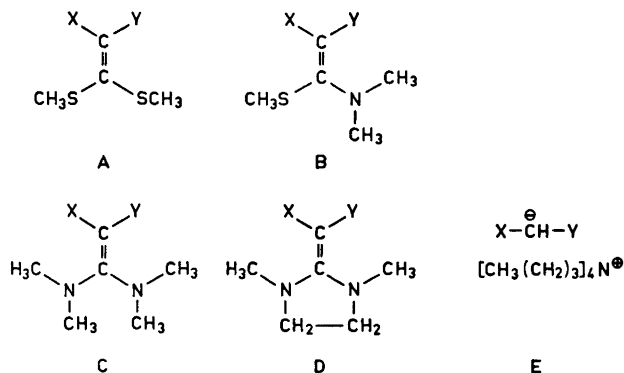
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The ultraviolet spectra of a number of ethylenes with push-pull substituents have been measured and interpreted with the aid of two modifications of Pariser-Parr-Pople SCF-MO calculations. Solvent effects are discussed from both experimental and theoretical points of view. The electronic absorption spectra of the anions of methylene active compounds with the same electron-accepting groups as the ethylenes were recorded. The charge distributions and bond orders in four compounds are discussed in relation to experimental data.

Ethylenes with both electron-donating and electron-accepting groups exhibit absorption bands in the near ultraviolet region characteristic of the delocalisation of the  $\pi$ -electrons throughout the molecule. Nagakura<sup>1</sup> has studied ethylenes with a nitro or carbonyl group as the electron-accepting group, and has assigned the absorption bands in these compounds to charge-transfer transitions. Loos *et al.*<sup>2</sup> have also studied intramolecular charge-transfer absorption in nitroethylenes from both experimental and theoretical points of view.

Investigations of the restricted internal rotation in ethylenes with push-pull substituents have been reported in previous parts<sup>3-5</sup> of this series. The present work was performed in order to study the ultraviolet spectra of these ethylenes both qualitatively and quantitatively. A UV study of the polarised ethylenes *1A, B, C, D - 10A, B, C, D* (see below) was therefore undertaken. To obtain a more quantitative understanding of the nature of the electronic transitions in these ethylenes, molecular orbital calculations were carried out on compounds *1A - 1D, 3A - 3D, 8A - 8D, and 10A - 10D* using the semi-empirical Pariser-Parr-Pople LCAO-SCF-MO method.<sup>6</sup> Furthermore a UV study of the tetrabutylammonium (Q) salts (*E*) or sodium salts of some of the active methylene compounds  $X-CH_2-Y$  was carried out.

\* Part IV, see Ref. 5.



	X	Y		X	Y
1.	CH <sub>3</sub> OCO	CN	6.	Ph	COCH <sub>3</sub>
2.	PhCO	CN	7.	PhCO	COCH <sub>3</sub>
3.	CN	CN	8.	CH <sub>3</sub> CO	COCH <sub>3</sub>
4.	<i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	CN	9.	CH <sub>3</sub> CO	CO <sub>2</sub> CH <sub>3</sub>
5.	Ph	CN	10.	CH <sub>3</sub> OCO	CO <sub>2</sub> CH <sub>3</sub>

## EXPERIMENTAL

Compounds *1A*, *C*, *D*–*10A*, *C*, *D* were prepared as previously described.<sup>3,7</sup> Gompper and Töpfl<sup>8</sup> have described the preparation of *1B*, and the preparation of *2B*, *3B*, *4B*, *5B*, *6B*, *7B*, and *10B* will be published in a forthcoming paper in this series. Compounds *8B* and *9B* were synthesized according to Ref. 9.

Table 1. Ultraviolet spectra of the anions X–CH–Y (E).

X	Y	λ <sub>max</sub> nm	ε
1. CH <sub>3</sub> OCO	CN	246 <sup>b</sup>	12600
2. C <sub>6</sub> H <sub>5</sub> CO	CN	242	6000
		251	4400
		317 <sup>a</sup>	7300
3. CN	CN	244 <sup>a</sup>	2800 <sup>c</sup>
4. <i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	CN	264	9100
		462	4600
		596 <sup>a</sup>	4800
7. PhCO	COCH <sub>3</sub>	248	6100
		310 <sup>a</sup>	12600
8. CH <sub>3</sub> CO	COCH <sub>3</sub>	245	2600
		274 <sup>a</sup>	9000
9. CH <sub>3</sub> CO	CO <sub>2</sub> CH <sub>3</sub>	272 <sup>b</sup>	18000
10. CH <sub>3</sub> OCO	CO <sub>2</sub> CH <sub>3</sub>	258 <sup>b</sup>	3200

<sup>a</sup> Tetrabutylammonium salt in CHCl<sub>3</sub>.

<sup>b</sup> Sodium salt in ethanol.

<sup>c</sup> Very approximate due to the hygroscopic nature of the salt.

Table 2. The observed wavelengths and molar extinction coefficients for compounds A, B, C, D in absolute ethanol.

X	Y	A		B		C		D	
		$\lambda_{\max}$ nm	$\epsilon$	$\lambda_{\max}$ nm	$\epsilon$	$\lambda_{\max}$ nm	$\epsilon$	$\lambda_{\max}$ nm	$\epsilon$
1. CH <sub>3</sub> OCO	CN	307	14 500	265	4 200	251	8 800	232 (sh)	10 400
				318	11 400	284	18 600	276	14 200
2. PhCO	CN	263	9 700	252	11 900	253 (sh)	12 200	251 (sh)	9 600
		349	11 100	346	13 600	320	14 400	310	12 000
3. CN	CN	300 (sh)	9 000	268 (sh)	6 000	243	9 400	240 (sh)	8 000
		330	13 900	307	15 500	276	18 200	262	15 700
4. <i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	CN	258	10 000	260	8 300	231	16 000	233	14 800
		292	9 000	287	8 800	290	10 800	294	7 800
		362	11 100	401	16 800	418	22 000	435	22 800
5. Ph	CN	234	8 200	230	9 600	235	13 400	229	12 700
		322	10 900	261	8 200	247	15 100	277 (sh)	8 400
				326	14 400	257 (sh)	11 800	317	16 600
						318	17 400		
6. Ph	COCH <sub>3</sub>	220 (sh)	9 300	227	7 200	225	7 800	235	6 600
		294	6 300	274	9 300	270 (br)	13 500	292	12 600
				357	8 800	340	13 800	318 (sh)	9 200
7. PhCO	COCH <sub>3</sub>	253	11 400	233	11 200	241	13 100	234	13 800
		318	8 700	271 (sh)	12 000	272 (sh)	12 400	290	14 400
				287	12 800	297	15 600		
				345	3 800				
8. CH <sub>3</sub> CO	COCH <sub>3</sub>	223	5 800	268	18 800	257	17 400	253	12 400
		317	8 200	272 (sh)	18 000	275	16 200	277	21 600
				350	1 400	292 (sh)	11 600		
9. CH <sub>3</sub> CO	CO <sub>2</sub> CH <sub>3</sub>	317	9 000	257	22 800	247	19 200	252	24 800
				345	2 800	299	7 500		
10. CH <sub>3</sub> OCO	CO <sub>2</sub> CH <sub>3</sub>	311	10 300	241	12 000	237	18 600	240	25 200
				265	7 000	293	12 400	274	6 200
				331	6 800				

sh = shoulder. br = broad.

Table 3. Experimental <sup>a</sup> and calculated ultraviolet spectra of compounds 1A-1D, 3A-3D, 8A-8D, 10A-10D.

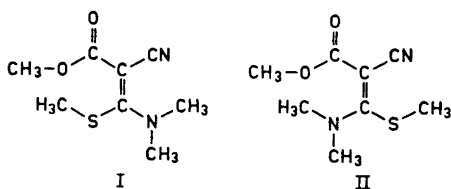
Compound	Experimental		Calculated <sup>b</sup>		Calculated <sup>c</sup>	
	$\lambda_{\max}$ nm	$\epsilon$	$\lambda_{\max}$ nm	$f$	$\lambda_{\max}$ nm	$f$
1A	300 (sh)	8 400	302.2	0.114	244.3	0.215
	327	12 200	319.1	0.215	273.7	0.359
1B I	265	5 600	235.3	0.187	228.5	0.173
	319	14 500	283.1	0.320	279.9	0.577
1B II			234.9	0.348	219.4	0.213
			292.5	0.237	272.1	0.510
1C	249	6 200	212.2	0.232	224.2	0.212
	290	15 800	266.2	0.486	281.5	0.590
1D	229 (sh)	7 700	213.8	0.244	225.1	0.265
	284	13 700	266.6	0.496	285.1	0.632
3A	292 (sh)	9 000	315.7	0.048	223.9	0.029
	324	13 200	330.5	0.263	265.3	0.554
3B	262	6 000	242.3	0.215	244.4	0.246
	310	13 300	298.4	0.280	279.6	0.663
3C	239	9 400	233.8	0.302	237.9	0.293
	282	19 200	275.6	0.472	282.5	0.689
3D	225 (sh)	8 700	231.9	0.311	239.7	0.323
	274	15 600	275.4	0.481	285.2	0.737
8A <sub>E-Z</sub>	309	7 400	321.4	0.111	261.7	0.175
			345.9	0.161	314.0	0.388
8A <sub>Z-Z</sub>			223.2	0.251	220.6	0.494
			337.3	0.044	288.3	0.036
			348.6	0.165	322.6	0.365
			218.7	0.289	219.5	0.585
8B <sub>E-Z</sub> III	246 (sh)	8 400	241.8	0.286	243.0	0.052
	264	14 400	312.9	0.168	297.1	0.560
	333 (sh)	5 400				
	352 (br)	5 200				
8B <sub>E-Z</sub> IV			216.6	0.373	226.6	0.246
			244.1	0.121	279.3	0.567
			296.0	0.242		
			222.3	0.353	220.0	0.548
8B <sub>Z-Z</sub>			249.7	0.109	251.7	0.079
			312.5	0.142	309.4	0.402
			222.9	0.320	238.2	0.289
			272.3	0.369	295.6	0.509
8C <sub>E-Z</sub>	254	15 800				
	264 (sh)	9 800				
	315	8 400				
8C <sub>Z-Z</sub>			228.8	0.313	252.3	0.239
			278.8	0.236	302.3	0.360
8D <sub>E-Z</sub>	252 (sh)	8 800	224.3	0.336	236.7	0.313
	270	13 200	272.0	0.376	293.1	0.544
	302 (sh)	3 000				
8D <sub>Z-Z</sub>			229.9	0.333	249.5	0.278
			278.2	0.241	300.2	0.383
10A	307	9 800	295.3	0.127	233.4	0.258
			327.1	0.144	303.1	0.332
10B V	279 (sh)	4 800	231.2	0.136	227.0	0.164
	313	11 000	275.2	0.248	295.1	0.493
10B VI			233.2	0.256	219.0	0.127
			298.3	0.160	279.3	0.450
10C	247 (sh)	8 200	202.4	0.180	235.6	0.177
	293	14 400	260.2	0.363	291.5	0.489
10D	232	17 400	203.8	0.203	235.1	0.232
	292	9 100	260.1	0.374	294.8	0.529

<sup>a</sup> In cyclohexane with 0.2 % dichloromethane. <sup>b</sup> Method 1. <sup>c</sup> Method 2. sh=shoulder. br=broad.

The preparation of the Q salts of the active methylene compounds was carried out according to the method of ion pair extraction described by Brändström *et al.*<sup>10</sup> The salt *3E* was very hygroscopic and had to be manipulated in a dry box. The identities of the anions were verified by NMR and by adding sulfuric acid to a water solution of the salt and recovering the active methylene compound, the identity of which was verified by IR. Unfortunately not all the desired Q salts (*1E*, *5E*, *6E*, *9E*, *10E*) could be prepared due to secondary reactions or insufficient acidity of the methylene compound. Therefore the UV spectra of the sodium salts of compounds *1E*, *9E*, and *10E* were recorded. The UV spectra of the anions are listed in Table 1.

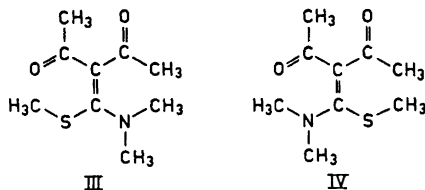
All the UV spectra were recorded on a Unicam Model SP 800 spectrometer. Absolute ethanol was used as solvent for compounds *1A*, *B*, *C*, *D*–*10A*, *B*, *C*, *D*. The spectra of the compounds used for comparison of calculated and experimental transition energies were also recorded in cyclohexane with 0.2 % dichloromethane. The peak wavelengths (nm) and molar extinction coefficients for all compounds in absolute ethanol are listed in Table 2. Experimental and calculated wavelengths (nm), molar extinction coefficients and oscillator strengths are tabulated in Table 3.

For all compounds *1* two conformations of the ester group are possible and NMR studies<sup>5</sup> of *9C* ( $X = \text{CO}_2\text{CH}_3$ ,  $Y = \text{COCH}_3$ ) show that the conformation with the ester carbonyl group  $E^{11}$  to the  $C=C$  bond is the most probable one. Assuming this to be valid also for compounds *1*, two conformations (I and II) can be formulated for *1B*.



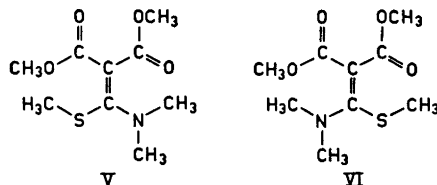
In the calculations these two conformations can be taken into account (see Table 3).

The acetyl groups in compounds *8* can have an *E*–*Z* arrangement, a *Z*–*Z* arrangement or an *E*–*E* arrangement with respect to the  $C-C=O$  bond. The *E*–*E* arrangement is not very likely because of strong dipolar repulsion between the carbonyl groups. Furthermore, NMR studies<sup>5</sup> of *8C* show that the conformation with the acetyl groups in an *E*–*Z* arrangement is dominant, but NMR studies of *8D* show that the conformation with *Z*–*Z* arrangement also exists. The conformation of *8B* which is *E*–*Z* with respect to the  $C-C=O$  bond can exist in conformations III and IV with respect to the  $C=C$  bond.



This can be taken into account in the calculations. In Table 3 the conformation with respect to the  $C-C=O$  bond is indicated with the indices *E*–*Z* and *Z*–*Z*, respectively.

For compound *10C*, only the *E*–*Z* conformation has been observed<sup>5</sup> and it is assumed to be at least the dominant one for *10A*, *B*, and *D* as well. Two forms, V and VI, must be considered for compound *10B*.



## MOLECULAR ORBITAL CALCULATIONS

The calculations have been performed by two somewhat different PPP methods. In all PPP methods the elements of the Fock matrix are given by

$$F_{\mu\mu} = H_{\mu\mu}^{\text{core}} - \frac{1}{2} q_{\mu} \gamma_{\mu\mu} + \sum_{\nu \neq \mu} q_{\nu} \gamma_{\mu\nu}$$

$$F_{\mu\nu} = \beta_{\mu\nu}^{\text{core}} - \frac{1}{2} p_{\mu\nu} \gamma_{\mu\nu}$$

The difference between the two PPP methods used in this work lies in the evaluation of the integrals.

*Method 1.* In this method the following expressions are used for the evaluation of the various integrals. The one-center repulsion integrals

$$\gamma_{\mu\mu} = I_{\mu} - A_{\mu}$$

where  $I_{\mu}$  and  $A_{\mu}$  are the valence state ionization potential and electron affinity of atom  $\mu$ . The two-center repulsion integrals are calculated according to the approximation given by Mataga and Nishimoto<sup>12</sup>

$$\gamma_{\mu\nu} = 14.40 / (R_{\mu\nu} + k_{\mu\nu}) \text{ eV}$$

where  $R_{\mu\nu}$  is the internuclear distance between atoms  $\mu$  and  $\nu$ , and  $k_{\mu\nu}$  is defined by

$$k_{\mu\nu} = 14.40 / [\frac{1}{2}(I_{\mu} - A_{\mu}) + \frac{1}{2}(I_{\nu} - A_{\nu})]$$

The core Coulomb integrals are calculated according to Goeppert-Mayer and Sklar<sup>13</sup>

$$H_{\mu\mu}^{\text{core}} = W_{\mu\mu} - (n_{\mu} - 1)\gamma_{\mu\mu} - \sum_{\nu \neq \mu} n_{\nu} \gamma_{\mu\nu}$$

where  $n_{\nu}$  is the number of electrons contributed to the delocalized  $\pi$ -system by the  $\nu$  atom.

In this method the expression

$$W_{\mu\mu} - (n_{\mu} - 1)\gamma_{\mu\mu}$$

is approximated by the ionization potential ( $I_{\mu}$ ) of the atom  $\mu$ .

The core resonance integrals  $\beta_{\mu\nu}^{\text{core}}$  are treated in some cases (see Table 4) as empirical parameters, the values of which have been determined to give a good fit between the experimental and calculated UV data, and in some cases by the expression first proposed by Mulliken<sup>14</sup> and then modified to a relationship of the type<sup>15</sup>

Table 4. Parameters used in PPP method 1.

Atom	$W_{\mu\mu}$ eV	$\gamma_{\mu\mu}$ eV	Ref.	Bond	Bond length Å	$\beta_{\mu\nu}$ eV
C	-11.42	10.84	17	C-C	1.39 <sup>d</sup>	-2.24
S	-20.40	10.84	17	C-C	1.44 <sup>e</sup>	-2.12
O	-26.73	14.58	17	C-C	1.45 <sup>e</sup>	-2.05
				C-S	1.74 <sup>d</sup>	-0.90 <sup>a</sup>
Ö	-16.86	15.23	18, 19	C-N <sup>b</sup>	1.33 <sup>d</sup>	-2.73 <sup>a</sup>
N	-28.71	16.75	19	C-N <sup>c</sup>	1.33 <sup>d</sup>	-2.90 <sup>a</sup>
C (nitril)	-11.19	11.09	19	C-N	1.14 <sup>d</sup>	-2.95 <sup>a</sup>
				C-Ö	1.25 <sup>e</sup>	-3.49
N (nitril)	-14.18	12.52	19	C-Ö	1.28 <sup>f</sup>	-3.09

<sup>a</sup> Adjusted values. <sup>b</sup> Compounds C. <sup>c</sup> Compounds D. <sup>d</sup> Taken from X-ray structure.<sup>20</sup>  
<sup>e</sup> Evaluated from HMO calculations with  $\alpha, \beta$ -variation. <sup>f</sup> Evaluated from PPP calculations.

$$\beta_{\mu\nu} = - \frac{S_{\mu\nu}}{1 + S_{\mu\nu}} \cdot \frac{I_{\mu} + I_{\nu}}{2}$$

where  $S_{\mu\nu}$  are the overlap integrals, evaluated according to Mulliken *et al.*<sup>16</sup>

The parameters used in this method are tabulated in Table 4. An idealized geometry was assumed, with all bond angles equal to 120° except for the compounds D where the N-C-N bond angle was taken to be 110° according to an X-ray crystallographic examination<sup>20</sup> of 1,3-dimethyl-2-(*p*-bromobenzoyl-cyanomethylene)-imidazolidine. Some of the bond lengths (see Table 4) were estimated according to the expression formulated by Coulson<sup>21</sup> using the values of bond orders obtained from HMO calculations with  $\alpha, \beta$ -variation<sup>22</sup> and PPP calculations, and some of the bond lengths were taken from the X-ray structure determination<sup>20</sup> of the *p*-bromo analogs of 2A and 2D.

*Method 2.* This method is a modified PPP approximation proposed by Roos and Skancke.<sup>23</sup> Evaluation of the integrals is performed in conformity with the following expressions. The one-electron core integrals  $W_{\mu\mu}$  are assumed to depend on the environment of atom  $\mu$  and this gives

$$H_{\mu\mu}^{\text{core}} = W_{\mu\mu} - (n_{\mu} - 1)\gamma_{\mu\mu} - \sum_{\nu \neq \mu} n_{\nu} \gamma_{\mu\nu}$$

$$W_{\mu\mu} = W_{\mu\mu}^{\circ} + \sum_{\nu} [\Delta W_{\mu}^{\circ}(\nu) + \delta_{\mu\nu}^W (R_{\mu\nu} - R_0)]$$

where the summing is over all neighbours to atom  $\mu$ .  $\Delta W_{\mu}^{\circ}(\nu)$  is the correction due to the replacement of a hydrogen atom by the atom  $\nu$ .  $R_{\mu\nu}$  is the internuclear distance between atoms  $\mu$  and  $\nu$ , and  $R_0$  is a suitably chosen standard length of the bond  $\mu\nu$ .

The core resonance integrals,  $\beta_{\mu\nu}$ , and the two-center repulsion integrals,  $\gamma_{\mu\nu}$ , between nearest neighbours also depend on the bond lengths, and linear relationships are assumed:

$$\beta_{\mu\nu} = \beta_{\mu\nu}^{\circ} + \delta_{\mu\nu}^{\beta} (R_{\mu\nu} - R_0) \text{ and}$$

$$\gamma_{\mu\nu} = \gamma_{\mu\nu}^{\circ} + \delta_{\mu\nu}^{\gamma} (R_{\mu\nu} - R_0)$$

The one-center repulsion integrals,  $\gamma_{\mu\mu}$ , have been estimated from spectral data,<sup>24</sup> and the ball approximation<sup>25</sup> has been used for calculating the two-electron two-center repulsion integrals,  $\gamma_{\mu\nu}$ , for non-neighbours.

Table 5. Parameters used in PPP method 2.

Atom	$W_{\mu\mu}^{\circ}$	$\gamma_{\mu\mu}$	Bond $\mu\nu$	$\beta_{\mu\nu}^{\circ}$	$\gamma_{\mu\nu}^{\circ}$	$\delta_{\mu\nu}^W$	$\delta_{\mu\nu}^{\beta}$	$\delta_{\mu\nu}^{\gamma}$	$\Delta W_{\mu\nu}^{\circ}$	$\Delta W_{\mu\nu}^{\circ}$	$R_0$ Å	Ref.
C	-9.84	11.97	C-C	-2.42	6.91	9.22	3.05	-3.99	0.07	0.07	1.397	26
$\dot{S}$	-10.62	9.58	C- $\dot{S}$	-1.37	7.28	9.22	3.05	-3.99	-0.70	0	1.714	27
$\dot{N}$	-12.57	15.44	C- $\dot{N}$	-2.72	7.16	5.6	2.6	-3.99	0.03	0.14	1.338	28
$\ddot{N}$	-8.52	15.44	C- $\ddot{N}$	-2.25	6.34	5.6	2.6	-3.99	0.03	0.14	1.338	28
$\dot{O}$	-19.60	18.89	C- $\dot{O}$	-2.46	9.33	0	0	0	-0.71	0	1.22	29
$\ddot{O}$	-11.18	18.89	C- $\ddot{O}$	-1.80	6.20	0	0	0	-0.09	1.51	1.35	30

The parameters used in this method are listed in Table 5. The geometries are the same as in method 1. The C $\equiv$ N group is not parametrized in this method, and therefore the parameters used for the nitrile nitrogen are those estimated for nitrogen of pyridine character.

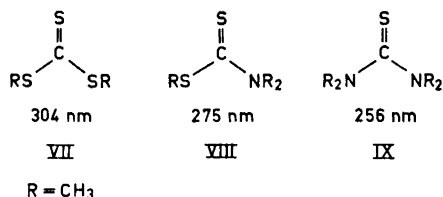
## RESULTS AND DISCUSSION

*General aspects on the experimental UV data.* The long wavelength absorption bands recorded in Table 2 have in most cases extinction coefficients higher than 6000 and should be ascribed to  $\pi \rightarrow \pi^*$  transitions. The only doubtful case is  $\delta B$ , for which the band at 350 nm ( $\epsilon = 1400$ ) could have been due to an  $n \rightarrow \pi^*$  transition in the carbonyl groups. However, the position of this band is hardly affected by changing the solvent from ethanol to cyclohexane (Table 3) which is contrary to the general behaviour of  $n \rightarrow \pi^*$  bands.

A certain analogy can be expected between the UV spectra of the compounds studied here and those of analogous thiocarbonyl compounds because of the resemblance in electronic effects between the group X-C-Y and the sulphur atom. However, this analogy cannot be stretched too far, since, when the groups X and Y have large  $\pi$ -electron systems, their influence on the light absorption will tend to overshadow that of the electron-donating groups. The thiocarbonyl compounds analogous to A-C are VII-IX, for which the  $\pi \rightarrow \pi^*$   $\lambda_{\max}$  values<sup>31</sup> are given below the formulas.

The order of  $\lambda_{\max}$ , decreasing with increasing electron-donating effect of the substituents at the thiocarbonyl group, is contrary to the qualitative resonance



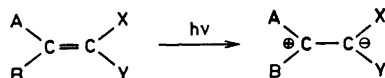


picture but is well supported by quantum chemical calculations.<sup>32</sup> In the series with X = CN, Y = CN (3) and X = PhCO, Y = CN (2) the same order of the wavelength maxima is observed. In all other series except 4 (X = *p*-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>, Y = CN) and 6 (X = Ph, Y = CN) the wavelengths increase in the order  $D < C < A < B$ .

It has been shown by NMR lineshape studies<sup>4</sup> and for one of the compounds (2D) also by X-ray crystallography<sup>20</sup> that the compounds *D* are twisted around the double bond in the ground state. This must affect the ultraviolet absorption spectra, and generally one should expect the absorption of the cyclic compounds *D* to be shifted further in the direction of the anions (X-CH-Y)<sup>-</sup> than those of *C*. To test this hypothesis, the Q salts or sodium salts of some of the active methylene compounds X-CH<sub>2</sub>-Y were prepared and their spectra recorded in chloroform or ethanol solution, respectively (Table 1). In the series 1, 3, 4, 8, 10, the above assumption is verified, whereas in 2 the spectra of *C*, *D*, and the anion are so similar that no trend can be observed. In 7 and 9 the cyclic diamines *D* absorb at shorter wavelength than both *C* and the anions. In 9D, however, the spectrum in chloroform shows a shoulder at 279 nm, and a corresponding band is probably present under the broad band at 252 nm in ethanol solution.

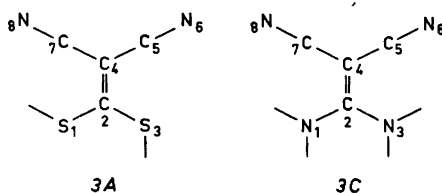
**Solvent effects.** If the degree of interaction between solvent and solute is relatively small there will be a bathochromic shift with increasing polarisability of the solvent.<sup>33,34</sup> In the following the shifts considered are those which occur on changing the solvent from cyclohexane to ethanol. Comparison of the UV spectra of compounds 1A-1D, 3A-3D, 8A-8D, and 10A-10D recorded in absolute ethanol and cyclohexane shows that 1,1-bis-alkylthioethylenes (*A*) and the solvent have the least interaction, except in compound 1A (X = CN, Y = CO<sub>2</sub>CH<sub>3</sub>), where there is a hypsochromic shift. 1B, 3B, and 8B are not affected by changing the solvent. However, in 10B there is a strong bathochromic shift. The compounds *C* and *D* absorb at shorter or the same wavelength when changing to a more polar solvent.

These results can be interpreted in the following way. The hypsochromic shifts and also the lack of shift in some compounds indicate that the polarity is decreased or reversed by the electronic transition, thereby weakening the interaction with polar solvents. In such cases the term charge-transfer band does not apply. The bathochromic shifts in some compounds of type *A* indicate some increase in polarity, but a change depicted as below evidently does not give a good description of the excitation mechanism. The only compound that shows a real charge transfer absorption is 10B, for which a bathochromic shift



of 18 nm is observed. Calculated charge densities (Table 6) for the ground state and the excited state for atoms 2 and 4 in compound 3A show that there is a slight increase of the polarity in the excited state, which confirms the

Table 6. Calculated <sup>a</sup>  $\pi$ -electron charges on the various atoms in compounds 3A and 3C in the ground and excited states.



	q <sub>1</sub>	q <sub>2</sub>	q <sub>3</sub>	q <sub>4</sub>	q <sub>5</sub>	q <sub>6</sub>
A Ground state	+0.046	-0.228	+0.046	+0.176	+0.114	-0.133
Excited state	+0.293	-0.373	+0.293	+0.151	+0.039	-0.220
C Ground state	+0.136	+0.047	+0.136	-0.312	+0.089	-0.182
Excited state	+0.228	-0.234	+0.228	+0.211	+0.002	-0.215

<sup>a</sup> PPP method 2.

above prediction. In compound 3C a reversed polarity at atoms 2 and 4 is found on going from the ground state to the excited state, and this is in agreement with the observed hypsochromic shift.

*Discussion of PPP calculations.* The agreement between calculated and observed absorption maxima is at best fair. With systems 1 and 3, method 1 gives reasonable agreement and also the correct order:  $\lambda(A) > \lambda(B) > \lambda(C)$ . In the other systems no reasonable trend can be observed. Generally method 2 gives larger discrepancies than method 1, which may be due to the fact that the former method has not been parametrized for the present systems. Especially for systems C and D, steric effects, which have not been taken into account in the calculation, may contribute to some of the observed discrepancies. This does not apply to systems 3A, 3B, 3D, which should be free from steric effects.

*Discussion of  $\pi$ -electron charges and bond orders.* The charge and bond order diagrams (Fig. 1) are rather similar in the two methods of calculation. The main differences are the electron densities and bond orders in the C=O and C $\equiv$ N groups. These differences can be ascribed to the rather different  $W_{\mu\mu}$

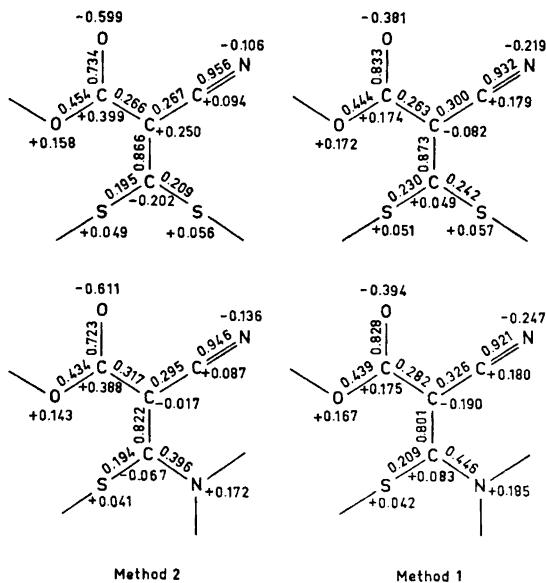


Fig. 1.  $\pi$ -Electron distributions and bond orders for the ground state of compounds 1A and 1B I calculated with both PPP methods (see text).

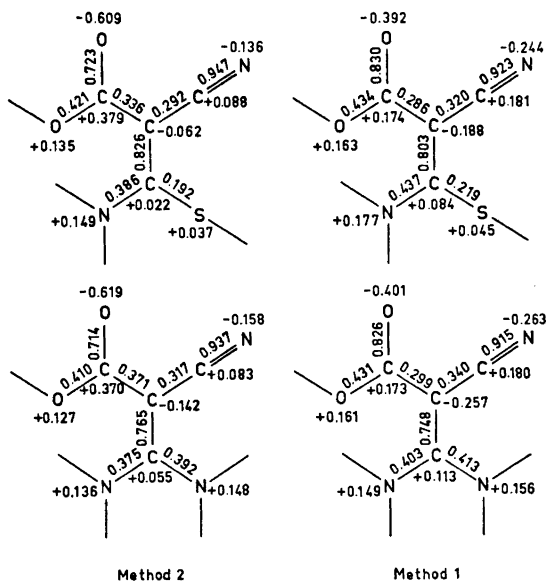


Fig. 2.  $\pi$ -Electron distributions and bond orders for the ground state of compounds 1B II and 1C calculated with both PPP methods (see text).

values for oxygen and nitrogen used in the two methods. It is also notable that method 2 gives a greater difference between the E and Z forms of *IB*. Otherwise, both series of diagrams show the expected increase in conjugation effects in the sequence *A*, *B*, *C*. The total positive charge on the electron-donating heteroatoms increases in this series, as does the negative charge on the electron-attracting oxygen and nitrogen atoms, whereas the bond order of the carbon-carbon double bond decreases. With method 1, the "local" dipole moment of the carbon-carbon double bond is always directed with the negative end towards the electron-attracting part of the molecule, whereas with method 2 the double bond in *IA* is quite strongly polarised in the opposite direction. In *IB* the E and Z forms have small polarities in opposite directions, and the double bond polarity in *IC* is in the direction of the overall dipole moment. The same charge relations are observed with compounds *3A* and *3C* (see Table 6 for results with method 2). Which set of results is the more realistic cannot be decided at present, since the dipole moments reveal only the sum of all charge displacements.

*Acknowledgements.* The author thanks professor Jan Sandström for his stimulating interest in this work and for valuable comments on the manuscript. Thanks are also due to Ingenjör Arne Rosdahl for experimental assistance. Financial support by the *Swedish Natural Science Research Council*, *Kungliga Fysiografiska Sällskapet i Lund*, and by *Fonden för ograduerade forskares vetenskapliga verksamhet* of the University of Lund is gratefully acknowledged.

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Received June 21, 1972.